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# Modeling of axial heterostructure formation in ternary III-V nanowires

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**Abstract.** A model is proposed to depict the formation of axial heterostructure in ternary III-V nanowires (NW) grown by the catalytic vapor-liquid-solid (VLS) method. Our approach is based on the determination of chemical potential of a four-component liquid using the regular solution model and Stringfellow's scheme for the computation of the interaction coefficients of species present in the droplet. The model allows the estimation of the heterojunction width dependence on the growth temperature. This dependence has not been reported before by any previous theoretical studies. The AlGaAs/GaAs heterojunction formation in the Au-catalyzed AlGaAs NWs was considered as an example of ternary system. The heterojunction width was found to increase with the growth temperature with a second-order polynomial dependence.

## 1. Introduction

Heterostructure nanowires (NWs) have a wide range of potential applications in opto- and nanoelectronics where the presence of an abrupt heterojunction is highly desirable for designing devices with high-performance characteristics [1, 2]. Vapor-liquid-solid growth (VLS) is probably the method most used to synthesize NWs [3] because it facilitates the formation of relatively sharp interfaces for several III-V semiconductors, elements from group V may be easily interchanged (e.g. InAsP/InAs, GaAsP/GaP [4]). In turn, the formation of abrupt interfaces is much more difficult (e.g. for AlAs/GaAs, GaInAs/InAs, InGaAs/GaAs [4]) when elements from group III are interchanged. This difference of interface sharpness has been explained by the fact that solubility of group III atoms in the catalyst droplet (10-40%) is usually higher than that of group V atoms, e.g. arsenic and phosphor (1-6%) [5]. Sophisticated growth techniques have been proposed to decrease heterojunction widths. For instance, a growth method with pulsed switching of material source was recently developed [6] resulting in a decrease of the heterojunction width down to 5-10 nm. Despite the variety of experimental data, theoretical studies to describe heterojunction formation in NWs are very limited [7-10]. To the best of our knowledge, none of the existing model deals with heterostructures in ternary III-V NWs. Moreover, only a small set of materials can be considered within the assumptions made. In reports describing the Si/Ge heterostructure formation in Au-catalyzed NWs [7-9], the material balance equations were considered for a fixed droplet volume, i.e. the amount of material coming into the droplet from the vapor is equal to the amount of material coming through the droplet-NW interface, albeit the droplet volume is not a constant in the general



case. The equilibrium concentrations of dissolved materials were determined by means of pseudo-binary [7] and pseudo-ternary [8] phase diagrams. This simplification was direct consequence of the difficulty to calculate accurately multicomponent system phase diagrams. Nevertheless, for a proper description of III-V NW growth, it is important to consider a concentration change for all materials [5, 11, 12].

In this paper, we propose a model describing heterostructure formation in ternary III-V NWs grown by catalytic VLS method. Our approach is based on the determination of chemical potentials of dissolved materials using the regular solution model and the Stringfellow formula for the computation of the interaction coefficients of species present in the droplet [5, 11]. In contrast to the existing works where only a three-component liquid droplet was considered, the model developed here utilizes a four-component liquid droplet, i.e. three NW growth materials and one catalyst. Furthermore, the droplet volume is not a fixed constant but can vary during the heterojunction formation. As a result, the model allows the estimation of the heterojunction width dependence on the growth temperature that was not demonstrated in previous theoretical reports. In what follows, the Au-catalyzed AlGaAs/GaAs NWs grown by the molecular beam epitaxy method are considered as an example of ternary system. The data presented in the literature [13] are used to compare our calculations with experimental results.

## 2. Model

In the model proposed, we assume that NW growth proceeds in a mononuclear layer-by-layer growth regime, in line with the case for NWs with small radii and under the usual conditions for molecular beam epitaxy NW growth [14]. The material fluxes from the vapor phase dissolve in the catalyst droplet and reach the droplet-NW interface. If the solution is saturated, two-dimensional islands (nuclei of solid phase) form at the interface. In the case of mononuclear nucleation, the lateral growth rate of islands is high and a complete monolayer forms before the next sequence of nucleation [14, 11, 12]. The driving force behind nucleus formation is a deviation from the chemical equilibrium condition [15]:  $\Delta\mu \equiv \sum v_j \mu_j = 0$ , where  $\mu_j$  is the chemical potential of the material involved in the chemical reaction and  $v_j$ , the stoichiometric coefficient. Our model accounts for AlAs and GaAs nuclei formation. Therefore, two reactions were considered:  $Al + As \rightarrow AlAs$  and  $Ga + As \rightarrow GaAs$ , respectively. Two variations of the chemical potentials were also introduced:  $\Delta\mu_{AlAs} = \mu_{Al}^L + \mu_{As}^L - \mu_{AlAs}^S$ ,  $\Delta\mu_{GaAs} = \mu_{Ga}^L + \mu_{As}^L - \mu_{GaAs}^S$ , where  $\mu_{Al}^L, \mu_{Ga}^L$  and  $\mu_{As}^L$  are the chemical potentials of Al, Ga and As in the droplet,  $\mu_{AlAs}^S$  and  $\mu_{GaAs}^S$  are the AlAs and GaAs chemical potentials in solid state. The Gibbs-Thomson effect was neglected since the correction to the chemical potentials is small for the radii to be considered (about 30 nm). For the calculation of the chemical potentials in the droplet, we considered the liquid as a regular solution. For Al atoms, for example, the chemical potential of is written as:  $\mu_{Al}^L = \mu_{Al}^{0L} + k_B T \ln a_{Al}$  where  $\mu_{Al}^{0L}$  is the chemical potential of pure Al,  $k_B$  - the Boltzmann constant,  $T$  - the growth temperature,  $a_{Al}$  - the Al activity in the four-component solution such that

$$k_B T \ln a_{Al} = k_B T \ln c_{Al} + \omega_{AlGa} c_{Ga}^2 + \omega_{AlAs} c_{As}^2 + \omega_{AlAu} c_{Au}^2 + c_{Ga} c_{As} (\omega_{AlGa} + \omega_{AlAs} - \omega_{GaAs}) + c_{Ga} c_{Au} (\omega_{AlGa} + \omega_{AlAu} - \omega_{GaAu}) + c_{Au} c_{As} (\omega_{AlAs} + \omega_{AlAu} - \omega_{AuAs}), \quad (1)$$

$c_{Al}, c_{Ga}$  and  $c_{As}$  are the Al, Ga, As molar fractions,  $\omega_{AlGa}, \omega_{AlAs}, \dots$  - the energy coefficients that allows for pair interactions between species. The energy coefficients are calculated using the Stringfellow formula [16]

$$\omega_{XY} = \frac{1}{N_A} \frac{V_X V_Y}{c_X V_X + c_Y V_Y} \left[ (\delta_X - \delta_Y)^2 - \frac{C(\chi_X - \chi_Y)^2}{(V_X V_Y)^{1/2}} \right], \quad (2)$$

where  $V_X$  is the molar volume,  $\delta_X$ , the Hildebrand solubility parameter,  $\chi_X$ ; the Pauling electronegativity constant,  $N_A$ , the Avogadro constant,  $C = 1.256 \times 10^5$  if all quantities are in SI units.

To find the chemical potentials in solid state,  $\mu_{AlAs}^S$  and  $\mu_{GaAs}^S$ , tabular values from the computations were used [17,18].

The Gibbs free energies of AlAs and GaAs island formation on the droplet-NW interface have the form of  $G_k = a_k i^{1/2} - \Delta\mu_k i$ ,  $k = \text{AlAs, GaAs}$ , where  $i$  is the number of AlAs or GaAs pairs in the nucleus,  $a_k = 2^{3/2}(\pi h_{ML} \Omega)^{1/2} \gamma_k$  (for disk-shaped nuclei),  $\gamma_k$ , the surface energy of nucleus side walls,  $h_{ML}$ , a monolayer height,  $\Omega$ , volume per atom. For the mononuclear growth, the NW growth rate in monolayers equals to the number of AlAs and GaAs nuclei that appear on the NW top facet per second [14]  $dL/dt = \pi R^2 (I_{AlAs} + I_{GaAs})$ , where  $I_k = A_k \exp(-a_k^2 / (4k_B T \Delta\mu_k))$  is the intensity of AlAs and GaAs island formation. Two intensities are summed since the AlAs and GaAs nucleation events are considered as independent. The factor  $A_k$  is a slow function (compared with the exponent) of atomic concentrations of species in the droplet and temperature. For simplicity, it was assumed that  $A_{AlAs} = A_{GaAs} = A$ , i.e. in the model the island formation intensity of AlAs and GaAs differ in strong exponential dependence only. The NW radius  $R$  is a constant since it does not change during the heterojunction formation in the experiment [13].

The lateral growth of the nucleus proceeds by attaching Al, Ga, As atoms from the liquid. The incorporation rate of Al and Ga atoms into the growing monolayer is proportional to the differences of corresponding chemical potentials:  $v_{Al} = b_{Al} \Delta\mu_{AlAs}$ ,  $v_{Ga} = b_{Ga} \Delta\mu_{GaAs}$  [19, 9],  $b_{Al}$  and  $b_{Ga}$  are kinetic coefficients. Therefore, the Al and Ga molar fraction in the growing monolayer can be presented in the following form:

$$X_{Al} \equiv \frac{v_{Al}}{v_{Al} + v_{Ga}} = \frac{\Delta\mu_{AlAs}}{\Delta\mu_{AlAs} + b_{Ga} / b_{Al} \Delta\mu_{GaAs}}, \quad X_{Ga} \equiv \frac{v_{Ga}}{v_{Al} + v_{Ga}} = 1 - X_{Al}. \quad (3)$$

Note that a monolayer composition is not influenced by the critical nucleus composition because its lateral size is much less than the NW radius. The material balance equations for material fluxes in and out of the droplet are derived on the basis that the chemical potential differences of species depend strongly on Al, Ga and As concentrations [5], leading to:

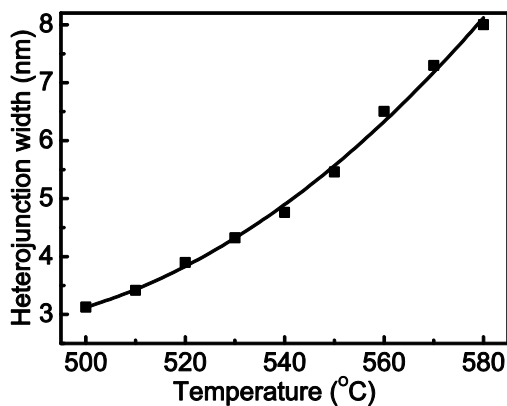
$$\begin{aligned} \frac{dN_{Al}}{dt} &= J_{Al} s(\alpha, \beta) - \frac{1}{2} \frac{dL}{dt} X_{Al}, \\ \frac{dN_{Ga}}{dt} &= J_{Ga} s(\alpha, \beta) - \frac{1}{2} \frac{dL}{dt} (1 - X_{Al}), \\ \frac{dN_{As}}{dt} &= J_{As} s(\alpha, \beta) - \frac{1}{2} \frac{dL}{dt} - s_t(\beta) \frac{c_{As}}{\tau_{As}}, \end{aligned} \quad (4)$$

Where  $N_{Al}, N_{Ga}, N_{As}$  are the number of Al, Ga and As atoms in the droplet divided by the number of atoms in one monolayer ( $N_{ML} = h_{ML} \pi R^2 / \Omega$ ), respectively.  $J_{Al}, J_{Ga}, J_{As}$  are the molecular fluxes of Al, Ga and As species (in monolayer/s).  $\tau_{As}$  is the desorption time for As atoms,  $s(\alpha, \beta)$ , part of the surface area of the droplet which the molecular fluxes intersect with [20] divided by  $\pi R^2$  (the droplet has a spherical cap shape).  $\alpha$  is the incidence angle of molecular beams (0 in this model),  $\beta$ , the droplet contact angle and  $s_t(\beta) = 2 / (1 + \cos \beta)$ , the total surface area of the droplet divided by  $\pi R^2$ . To obtaining the formulae in equation (4), the differences in atomic volumes in liquid and solid state between Al, Ga and As atoms were neglected ( $\Omega_{Al} \approx \Omega_{Ga} \approx \Omega_{As}$ ). Evaporation of group III atoms are negligible [21, 22] and thus, the desorption time for As atoms only is introduced. The growth rate  $dL/dt$  and the monolayer composition  $X_{Al}$  are a function of the molar fractions  $c_{Al}, c_{Ga}$  and  $c_{As}$  which equal to  $c_l = N_l / (N_{Au} + N_{Al} + N_{Ga} + N_{As})$ ,  $l = \text{Al, Ga, As}$  by definition. Therefore, equation (4) is a system of ordinary differential equations with three unknown functions  $N_{Al}, N_{Ga}, N_{As}$  ( $N_{Au}$  is

fixed). As initial conditions,  $N_{Al}^0, N_{Ga}^0$  and  $N_{As}^0$ , a steady state regime system solution is used, i.e.  $dN_{Al}/dt = dN_{Ga}/dt = dN_{As}/dt = 0$ .

### 3. Results and discussion

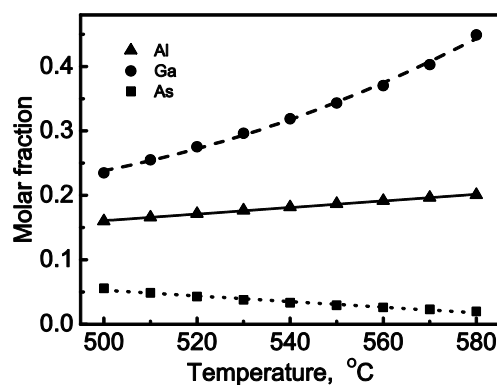
The model enables us to find the dependence of the heterojunction width on the growth temperature. For this purpose, it is essential to estimate the values of the material constants and how they vary with the temperature. In the general case, the following constants:  $A$ ,  $\tau_{As}$ ,  $b_{Al}$ ,  $b_{Ga}$ ,  $\Omega$ , are dependent on the temperature.  $A$  has an exponential temperature dependence where it is believed that the argument of the exponent is small enough to neglect this dependence [22]. The desorption time of As equals to  $\tau_{As} = \tau_{As0} \exp(E_{des}/k_B T)$  [3].  $E_{des} \approx 0.5$  eV was estimated from the saturated vapor pressure dependence of As on the temperature [24]. The term  $b_{Al}/b_{Ga}$  reflects the ratio of two Avogadro dependences with  $(E_{des}^{(Al)} - E_{des}^{(Ga)})/k_B T$  as an argument [19], where  $E_{des}$  is the energy barrier for atoms incorporating to the growing monolayer from the droplet. We suppose that this ratio has a weak dependence on temperature since the difference,  $E_{des}^{(Al)} - E_{des}^{(Ga)}$ , should be small in  $k_B T$  units. Likewise for a simplified consideration,  $b_{Al}/b_{Ga} = 1$ . The surface energy of the nucleus side facets should be a slow linear function of the temperature and this dependence can be neglected in the fraction  $\gamma_k^2/\Delta\mu_k$ , where  $\Delta\mu_k$  has a stronger polynomial dependence on  $T$  [5]. Given the exact values of the surface energies of nanoislands are unknown, the following simplification was made to account for the difference in AlAs and GaAs surface energies:  $\gamma_{AlAs} = 1.2\gamma_0$  and  $\gamma_{GaAs} = \gamma_0$ , where the factor 1.2 is a typical ratio between the AlAs and GaAs surface energies [3,23] and  $\gamma_0$  is left as a fitting parameter. Change in  $\Omega$  is negligible for the considered temperature range (500–600 °C). As a result, there are three fitting parameters in the model:  $A$ ,  $\tau_{As0}$  and  $\gamma_0$  that are determined from a comparison with the experimental data [13]. In the experiments, AlGaAs NWs with embedded GaAs quantum well were grown. The substrate temperature was fixed and equal to 550 or 580 °C. The  $As_4/(Ga + Al)$  flux ratio was set at 1. The nominal speed of growth (i.e. growth of a pure surface) was chosen equal to 1 monolayer per second for GaAs and 0.4 of monolayers per second for AlAs. The Al content along the NW was monitored by Raman spectroscopy. It was found that Al concentration was in the range of 0.24–0.26 while the NW radius was 20–30 nm.



**Figure 1.** AlGaAs/GaAs heterojunction width as a function of the growth temperature. The solid line is the best-fit function  $h = 103 - 0.4T + 4.5 \cdot 10^{-4} T^2$ , where  $h$  is the heterojunction width.

To compute the AlGaAs/GaAs heterojunction width at the temperature  $T$ , equation (4) is solved when  $J_{Al}$  is turned off ( $J_{Al} = 0, J_{Ga} \neq 0, J_{As} \neq 0$ ) and the numbers  $N_{Al}^0, N_{Ga}^0, N_{As}^0$  from the steady state

regime are used as initial conditions. To estimate the number of Au atoms  $N_{Au}$ , it is assumed that if the contact angle  $\beta$  equals  $90^\circ$ , the percentage of Au atoms is in the range of 50-80% [5], leading to  $N_{Au} = 50N_{ML}$  in the computations. The results of the modelling are presented in figure 1, where the condition  $X_{Al}(t) < X_{Al}(t=0)/e$  are used as a criterion that the heterojunction has formed (i.e. the Al flux is turned off at  $t=0$ ). The following values of the fitting parameters ( $A=11.3 \text{ nm}^{-2}\text{s}^{-1}$ ,  $\tau_{As0}=3.2\times 10^{-6} \text{ s}$ ,  $\gamma_0=0.2 \text{ J}\cdot\text{m}^{-2}$ ) enabled us to obtain the heterojunction width and the NW growth rate similar to those in the experiment (about 3 nm and 1 nm/s, respectively). For comparison,  $A\approx 0.5 \text{ nm}^{-2}\text{s}^{-1}$ ,  $\gamma_0\approx 0.1 \text{ J}\cdot\text{m}^{-2}$  were reported in the literature [22] to describe the formation of GaAs self-catalyzed NWs.



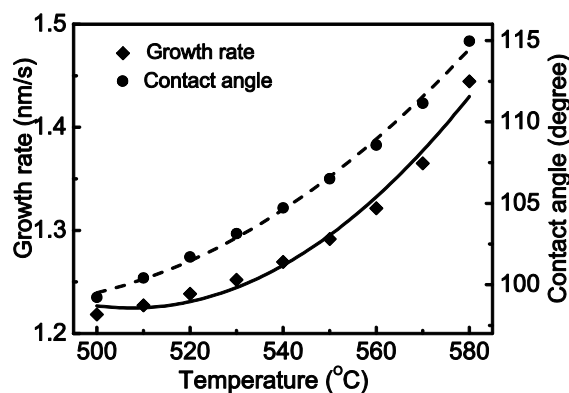
**Figure 2.** Al, Ga and As molar fractions versus the growth temperature. The lines are the best-fit functions

$$c_{Al} = -0.094 + 5.1 \cdot 10^{-4} T,$$

$$c_{Ga} = 3.1 - 0.013T + 1.4 \cdot 10^{-5} T^2$$

$$\text{and } c_{As} = 0.27 - 4.4 \cdot 10^{-4} T.$$

An increase of the heterojunction width from 4.1 nm to 7.7 nm (88% increase) when the temperature was varied from  $500^\circ\text{C}$  to  $580^\circ\text{C}$  is attributable to the increase of the number of Al atom  $N_{Al}$  in the droplet (108%). Although the change of the Al molar fraction (figure 2) is only 25%, the variation of the Ga molar fraction is much larger (91%) and results in a significant change of the droplet volume (66% increase that corresponds to the contact angle  $\beta$  change from  $99^\circ$  to  $115^\circ$  (figure 3) that leads finally to the increase of  $N_{Al}$ . The NW growth rate does not change much (increases by 18%, see figure 3) and equals to 1.2-1.4 nm/s. Thus, the values of heterojunction width and growth rate obtained in the model are similar to those in the experiment.



**Figure 3.** The dependence of NW growth rate and contact angle on the growth temperature. The lines are the best-fit functions  $h_{ML} dL/dt = 11 - 0.04T + 3.9 \cdot 10^{-5} T^2$  and  $\beta = 438 - 1.4T + 1.5 \cdot 10^{-3} T^2$ .

It was found that the heterojunction width, contact angle, growth rate and Ga molar fraction increase with the temperature as second-order polynomial functions (figure 1, 2 and 3) but the Al and Ga molar fraction show a close to linear dependence on the temperature (figure 2).

#### 4. Conclusion

A model of heterostructure formation in ternary III-V NWs grown by catalytic VLS method is presented. The approach proposed is based on the determination of chemical potential of a four-component liquid using the regular solution model and Stringfellow's scheme for the computation of the interaction coefficients of species. The AlGaAs/GaAs heterojunction formation in AlGaAs NWs was described using the model. Although the calculations were performed for the particular case of ternary material system, the model may be extended to other ternary III-V systems. In contrast to the previously developed models, the droplet volume can vary during the heterojunction formation. The heterojunction width was found to increase with the growth temperature with a second-order polynomial dependence. Another advantage of the model is an ability to describe both the steady-state and transient regime of NW growth. These results can be used for further improving of the NW growth techniques, e.g. for the optimization of the growth method with pulsed switching of material sources.

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